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LASER STUDIES OF MOLECULAR DYNAMICS(U) IBM THOMAS J
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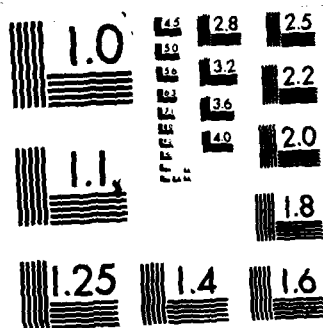
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LASER STUDIES OF MOLECULAR DYNAMICS

FINAL REPORT

P. P. Sorokin, Chief Investigator

December 5, 1983

U.S. Army Research Office

DAAG29 80 C 0131

**IBM Thomas J. Watson Research Center
Yorktown Heights, New York 10598**



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INTRODUCTION

Several objectives outlined in the original technical proposal (see IBM Technical Proposal: Laser Studies of Molecular Dynamics) were fulfilled in the work done under the three-year contract (25 August 1980 - 24 August 1983). A comparison of results that were actually achieved with our stated goals serves as the structure for this final report. Results are presented roughly in the order they were obtained.

Study of Laser-Initiated Explosions in HN_3

We used an improved version of time-resolved infrared spectral photography (TRISP) to study CO_2 laser-induced thermal explosions of gas phase HN_3/DN_3 mixtures.¹ HCl gas added to the mixtures was utilized to probe the transient temperature of the reaction. An induction period and a phase of rapid energy release were clearly identified and characterized both with respect to temperature and utilization of reactant material. Initiation of HN_3 explosions by laser beams was suggested as a topic for TRISP study in our original proposal. Chemical laser possibilities of the HN_3 decomposition reaction were not thoroughly investigated. However an attempt to construct an $\text{N}_2\text{-CO}_2$ transfer laser based upon this reaction proved unsuccessful.

Time-Resolved Infrared Study of Free Radicals in the Gas Phase

Using TRISP, we observed for the first time the gas phase IR spectrum of tertiary-butyl radicals and accurately measured their bimolecular rates of combination and disproportionation.²⁻³ The radicals were prepared by ruby laser photolysis of monomeric $(\text{CH}_3)_3\text{CNO}$ gas. TRISP spectra were recorded photoelectrically for the first time in this study, which allowed quantitative absorbance measurements to be made. Study of transient radical IR spectra by TRISP was one of the suggested topics in our proposal.

Laser Photolysis of Chlorine Dioxide

The technique of TRISP was utilized to elucidate the sequence of chemical events that follow the application of 308nm XeCl excimer laser pulses to chlorine dioxide (OClO) vapor.^{4,5} Both non-explosive^{4,5} and explosive⁵ regimes were studied. In the former case, gaseous chlorine perchlorate (ClOClO_3) was found to be a major photolysis product. Both its formation, as well as that of a transiently appearing molecule never before observed spectrally, chlorine sesquioxide (Cl_2O_3), were following in time with the aid of TRISP. The Cl_2O_3 was convincingly shown to form as an equilibrium association product of ClO radicals with OClO molecules. Although a different explanation of the origin of ClOClO_3 was initially offered⁵, we now believe, as a result of further measurements, that ClOClO_3 is formed by direct bimolecular reaction of ClO radicals with ClO_3 radicals. The latter have only been observed spectrally before as an IR absorbing metastable species formed at low temperatures in irradiated KClO_3 . The strong IR bands of ClO_3 are

the symmetric and anti-symmetric stretches located near $\sim 800\text{cm}^{-1}$. These two bands occur, unfortunately, at slightly longer wavelengths than the current long wavelength limit of TRISP ($\sim 900\text{cm}^{-1}$, see below). We hope to solidify our argument regarding the origin of ClOClO_3 with spectral proof sometime in the near future.

The explosive regime of OClO was quantitatively characterized and shown to be a chain reaction controlled by the bimolecular combination of ClO radicals.⁵

Extension of the Range of TRISP to $\sim 11\mu\text{m}$

With the use of a number of transitions in Cs and Rb vapor we extended the long wavelength limit of TRISP from $\sim 3\mu\text{m}$ to $\sim 11\mu\text{m}$. A table showing the Raman IR generators and upconverters actually used to obtain TRISP coverage of the 2- $11\mu\text{m}$ region appears in Ref. 5. This extension was absolutely required for study of the oxides of chlorine and was one of the projects originally suggested in our proposal.

Study of DABCO as a Two-Photon Laser

Since the start of the summer (1983) we have been investigating the possibility that an amplifier of picosecond light pulses based upon two-photon stimulated emission (TPSE) can be realized in DABCO vapor. This was the last topic suggested in our original proposal. Our scheme centered on using

the one-photon forbidden, two-photon allowed $\tilde{A} \rightarrow \tilde{X}(3s(+) \rightarrow n(+))$ transition of this molecule. Two-photon amplifying transitions could possibly occur between the zero vibrational level of the \tilde{A} state to several thermally unoccupied (symmetric) vibrational levels of the X state. The half frequencies for these transitions are all in the Rhodamine 6G dye laser range, making it particularly convenient for obtaining the $\sim 1\text{mJ}$, $\sim 1\text{psec}$ pulses we currently estimate are required to start a two-photon cascade. For TPSE from the \tilde{A} state to exceed one-photon absorption from the same state it is required that $\delta_{\text{TPSE}}\phi > \sigma_A$, where ϕ is the peak flux of the input pulse, δ_{TPSE} is the (resonant) two-photon cross-section for downward transitions at the input pulse frequency, and σ_A is the cross-section for linear absorption from the \tilde{A} state at the same frequency. A knowledge of excited state absorption in DABCO is thus obviously required. This was provided by the following technique. DABCO vapor was pumped to a higher state ($B, 3p_{x,y}(+)$) with a $\sim 1\text{J}$, 40nsec long, KrF laser pulse. Rapid ($< 10^{-8}\text{sec}$) interconversion to excited vibrational levels of the \tilde{A} state then occurred, and \tilde{A} state absorption ranging from $\sim 7500\text{\AA}$ to $\sim 4400\text{\AA}$ was then recorded with the aid of pulsed dye continua. The spectrum is observed to comprise discrete bands. The strongest bands were easily interpreted as belonging to a single, allowed, Rydberg series $3s(+) \rightarrow mp_{x,y}(+)$, $m \geq 4$. Since $\sigma_A(\nu) \approx 0$ except in the regions of these bands, which all appear to be Lorentzian, with spectral widths in the $\sim 50\text{cm}^{-1}$ range, the best frequencies to try TPSE now become apparent. A

quantitative determination of the Astate population was also made with a laser saturation technique. It showed that most of the absorbed KrF pump energy can be utilized to populate the \tilde{A} state, even in its lowest vibrational levels if an atmosphere of H_2 buffer gas is present.

Our present efforts are centered on seeing if it is possible to dump the \tilde{A} state population in its lowest vibrational state by TPSE induced by the application of ~ 1 mJ picosecond pulses resonantly tuned to the various allowed (downward) two-photon transitions. A detailed report⁶ on the above mentioned work is to be written soon.

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